PHYSICAL REVIEW B VOLUME 57, NUMBER 11 15 MARCH 1998-I

Electronic structure of acetylene on Si(111)-7×7: X-ray photoelectron and x-ray absorption spectroscopy

F. Rochet*
Laboratoire de Chimie Physique, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France
and Laboratoire pour L'Utilisation du Rayonnement Electromagnétique, Centre Universitaire Paris-Sud, Bâtiment 209D,
F-91405 Orsay Cedex, France

G. Dufour
Laboratoire de Chimie Physique, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France

P. Prieto† and F. Sirotti
Laboratoire pour L'Utilisation du Rayonnement Electromagnétique, Centre Universitaire Paris-Sud, Bâtiment 209D,
F-91405 Orsay Cedex, France

F. C. Stedile
Departamento de Físico-Química, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre, RS, Brazil

(Received 24 July 1997)

The electronic structure of acetylene adsorbed at room temperature on Si(111)-7×7, its thermal stability, and its reactivity in the presence of a silicon flux have been studied by synchrotron radiation x-ray photoemission of valence bands and core-levels (C $1s$, Si $2p$) and x-ray absorption spectroscopy (C K edge). We observe that the electronic occupancy of both adatoms and restatoms is modified by the adsorption process. The alignment of the C-C molecular axis by the chemisorption bond leads to a strong polarization dependence of the C K-edge spectra. The orientation of the C-C molecular axis is then determined to be nearly parallel to the surface plane and the bonding of di-σ type. Annealing sequences of an acetylene-saturated surface (up to a maximum temperature of 955 K) induce strong changes in the electronic structure of both molecule and substrate. There are hints of molecule/molecule reactions involving the in-plane π bond. We observe also the penetration of atomic carbon into the surface silicon layers, which in turn induces changes in the electronic structure of the silicon surface atoms. In the case of an exposure of an acetylene predosed surface to a silicon flux at 300 K, the molecule floats over the growing silicon layer, maintaining a di-σ bonding, as the in-plane π bond does not interact with incoming silicons. [S0163-1829(98)01311-3]

I. INTRODUCTION

Since about a decade the adsorption of acetylene on silicon surfaces [Si(111)-7×7,[1,2] Si(111)-2×1,[3] and Si(001)-2×1 (Refs. 4–6)] has received a continuous attention. Indeed this simple unsaturated hydrocarbon molecule is a promising carbon source for the homoepitaxial growth of 3C-SiC on 3C-SiC(001),[7] or its heteroepitaxial growth on a vicinal Si(001) surface[8] at temperatures below 1000 °C. But the interest is also of scientific order: the bonding of π-bonded hydrocarbon molecules on a reconstructed semiconductor surface is *a priori* different from its bonding on metal surfaces, on which their adsorption has been studied in great detail,[9] essentially because covalent surfaces undergo a considerable reconstruction, so that adsorption of molecules may alter to a great extent. Hence the determination of adsorption geometry on semiconductor surfaces may be not easy.

To our knowledge the adsorbed C_2H_2/Si(111)-7×7 system (at 300 K) was the matter of only two experimental works, based on high-resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM). The HREELS experiment of Yoshinobu *et al.*[1] pointed to the absence of characteristic Si-H vibration modes and thus to a nondissociative adsorption process. The vibrational mode seen at 1150 cm^{-1} was attributed to C-C stretching. Because the C-C single bond stretching mode has a typical value of 1100 cm^{-1} for the free ethane molecule, Yoshinobu and co-workers considered that the acetylene triple bond was rehybridized after adsorption to a state between sp^3 and sp^2 (di-σ bonding). The same group[4] found also a vibrational mode at 1090 cm^{-1}, after adsorption of acetylene on Si(001)-2×1, and interpreted the data as in Ref. 1, although the adsorption sites are *a priori* very dissimilar on each surface. Indeed there is no consensus for the interpretation of HREELS data. More recently Huang *et al.*,[5] studying the adsorption of acetylene on Si(001)-2×1, challenged the interpretation made by Yoshinobu and co-workers. They attributed an energy-loss peak at 1450 cm^{-1}—which remained until now unobserved—to the C-C stretching mode, that would be the signature of a carbon rehybridization to a sp^2 state. The controversy has not ceased yet: Chen *et al.*,[6] studying the C_2H_2/Si(001)-2×1 system, attribute, as Yoshinobu and co-workers, the 1090 cm^{-1} mode to the C-C stretching mode.

The STM work carried out by Yoshinobu *et al.*[2] on the

0163-1829/98/57(11)/6738(11)/$15.00

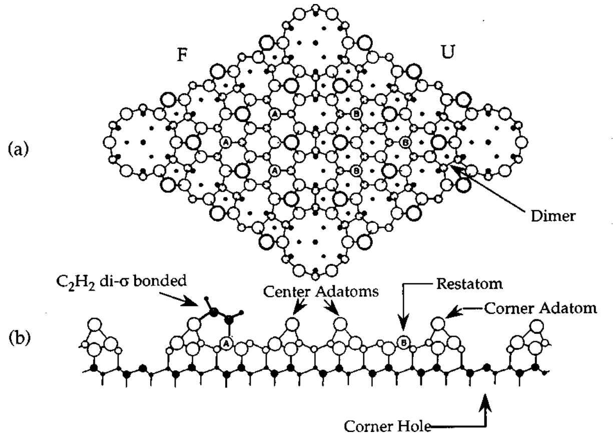

FIG. 1. (a) Top view and (b) side view of the DAS model of the Si(111)-7×7 surface. Each unit cell contains 12 adatoms, 6 restatoms, and one corner hole. Each adatom is bonded to three pedestal atoms. The deeper atoms are indicated as solid dots. The left triangle subunit shows a stacking fault (F). The right triangle is unfaulted (U). A molecule bridging a restatom and an adatom is also drawn (Yoshinobu's model).

adsorption of acetylene on Si(111)-7×7 has shown that the electronic occupancy of the adatoms (for a schematic picture of the ''dimer-adatom-stacking (DAS) fault'' model[10] see Fig. 1) varies upon C_2H_2 adsorption. It is also shown that the reactivity of adatoms in the faulted subunit is larger than that of those in the unfaulted one. Restatoms are not visible in the topographic images and their occupation is not probed by scanning tunneling spectroscopy. Yoshinobu and co-workers proposed again that C_2H_2 is di-σ bonded: the molecule would bridge two neighboring atoms bearing dangling bonds, i.e., a corner adatom and a restatom or a center adatom and a restatom, whose direct distances are 4.57 and 4.56 Å, respectively. Such a model (denoted now Yoshinobu's model) leads to a saturation coverage of 1 molecule/restatom (that is, 0.245 ML of carbon); only half the adatoms are involved in the bonding. We note that such a bridge site has already been proposed by Piancastelli *et al.*[11] in their STM study of the adsorption of ethylene on Si.

It is clear that the envisaged biradical sites for acetylene adsorption on the Si(111)-7×7 surface, present a Si-Si distance much larger than the corresponding ones on Si(001)2×1. On the latter surface the molecule can bridge either two dimerized Si (Si-Si distance around 2.5 Å) or a cleaved Si dimer (Si-Si distance around 3.8 Å). Theoretical works[12,13] favor the adsorption, on *uncleaved* Si-Si dimers, of a molecule distorted to an ethylenelike sp^2 configuration (C-C distances in the range of 1.33–1.36 Å). In view of the much larger bridging distance on Si(111)-7×7 with respect to that of Si(001)-2×1, one could expect either the C-C elongation to be greater on (111) than on (001), or a strong modification of the 7×7 reconstruction to occur upon adsorption (e.g., a displacement of adatoms). A semiempirical quantum chemical study[14] of acetylene reaction with the ''ideal'' Si(111)-1×1 surface suggests that sizeable rearrangement of the surface occurs, as Si-Si bonds are weakened or even broken, due to the strain induced by Si-C bond formation.

Consequently many unsolved questions remain about the structural determination of acetylene on Si(111)-7×7, which has been investigated until now essentially by vibrational spectroscopy. The present work, based on a study of the electronic structure of the adsorbate *and* substrate system, is therefore an original contribution to the issue. Indeed, we have monitored the changes in the electronic structure induced by the adsorption process combining synchrotron radiation x-ray photoemission spectroscopy (SRXPS) of valence bands and of core levels (C $1s$ and Si $2p$) and x-ray absorption spectroscopy (XAS) at the C K edge—also termed near-edge x-ray absorption fine-structure (NEXAFS) spectroscopy. On the one hand, SRXPS, performed in conditions of high surface sensitivity, is a powerful technique to follow the evolution of the surface silicon states and the bond formation[15] between Si and the C adsorbates. On the other hand, Stöhr, in his recent comprehensive book on NEXAFS,[16] has illustrated the ability of the technique to detect the presence of specific bonds in the molecules (e.g., C-C, C=C, C≡C, and C-H bonds) and to derive the molecular orientation.

The goal of this study was to determine the electronic structure of the molecule adsorbed at room temperature, its thermal stability and its reactivity in the presence of a silicon flux. We have evidenced that the occupancy of both adatoms and restatoms electronic levels is modified by the adsorption process. The bonding of the molecule to the surface is of di-σ type, with the C-C axis lying nearly parallel to the surface. We also discuss the consequences of a possible sp^3 hybridization of the carbon atoms, proposed by Yoshinobu and co-workers.[1] The heating of an acetylene-saturated surface between 300 and 955 K, leads to strong changes in the electronic structure of both molecule and substrate. We find hints for unexpected molecule/molecule reactions (polymerization, graphitization, etc.), related to the peculiar role played by the π orbital contained in the sample surface plane. We evidence also the penetration of C into the surface silicon layers, which in turn induces the formation of new silicon surface states. In the case of an exposure of an acetylene predosed surface to a silicon flux at 300 K, we observe that the in-plane ''π'' orbital does not open to bond with incoming Si atoms: the molecule floats over the growing silicon layer maintaining a di-σ bonding.

II. EXPERIMENT

A. Clean surface preparation and exposure to acetylene

The Si samples are prepared in the ultrahigh-vacuum (UHV) analyzing chamber whose base pressure is $\sim 10^{-10}$ Torr. The sample (a phosphorus-doped silicon wafer, of resistivity 0.002–0.005 Ω cm) is heated by the Joule effect: then temperature measurements are made by infrared pyrometry. The silicon wafer is cleaned of its silica protective layer by heating at ~1520 K, in order to minimize SiC contamination.[17] The surface cleanliness is checked by the intensity of the Si $2p$ core-level surface state, by a survey of the C $1s$ region, and by the sharpness of the low-energy electron diffraction (LEED) patterns.

Then the silicon surface is exposed to acetylene in the analysis chamber itself, under pressures in the range 10^{-6}–2.5×10^{-6} Torr. We use 99%-enriched C_2D_2 gas purchased from Eurisotop-CEA without further purification.

While the gas is introduced through a leak valve, the cryopump is isolated, and the chamber is evacuated by a turbomolecular pump. Acetylene pressures ($P_{\mathrm{acetylene}}$) are measured with an ionization gauge the reading of which was corrected by a sensitivity factor of 2 (the sensitivity factor is 1 for N_2). Exposures to the gas are given in Langmuir (L) units: 1 L corresponds to an exposure of 10^{-6} Torr s.

The *in-situ* exposure of the sample surface to a silicon flux was realized using an OMICRON EFM3 evaporator fitted with an integrated flux monitor, which allows a precise evaporation rate adjustment and control. The calibration of the cell has been made in a separate UHV chamber, by deposition of various Si amounts on a carbon substrate and their subsequent measurement by Rutherford backscattering spectrometry (RBS). The flux rate is 3.8×10^{14} Si atoms/cm^2/mn, with an absolute precision of $\pm20\%$, essentially due to the uncertainties in the measurement of the distance between the Si evaporant and target in both UHV chambers. Deposited Si amounts are given in ML units: 1 ML corresponds to 7.8×10^{14} atoms/cm^2.

B. X-ray photoemission

Photoelectron energy distribution curves are measured for valence bands VB's Si $2p$ and C $1s$ core levels with monochromatic synchrotron radiation and a partially angle-integrating electrostatic electron energy analyzer (RIBER MAC2). The linear polarization of the synchrotron radiation $\mathbf{E}$ is at 40° with respect to the axis of the cylindrical electron analyzer, defining an horizontal scattering plane. The sample surface is put in the common focus of the light beam and of the analyzer entrance lens and can be oriented about the vertical axis through the photoemission spot. The sample surface normal is always parallel to the analyzer axis and the light polarization vector is contained in the (110) plane of the Si(111) surface. The light source is the linear undulator DOMINO of beam line SU7 of the SuperACO storage ring. The undulator radiation is monochromatized by a 10-m toroidal grating monochromator covering the 130–800 eV photon range. Photons of energy 145 eV are used to excite the Si $2p$ core level of binding energy (BE) around 99 eV, in conditions of maximum surface sensitivity [for photoelectrons of kinetic energy around ~45 eV an escape depth of about 3.5 Å is estimated[18]]. The C $1s$ spectra (BE around 284 eV) are recorded at $h\nu=330$ eV, so that the kinetic energy of the C $1s$ photoelectrons equals that of the Si $2p$ photoelectrons. Valence bands are also measured at 145 eV.

In order to improve the resolution of the various components that contribute to the Si $2p$ spectra, the procedure given in Ref. 15 is followed. The background is first subtracted. Then the low j component of the Si $2p_{1/2,3/2}$ doublet is removed, mathematically (assuming identical shapes for the two components), with a branching ratio $2p_{1/2}:2p_{3/2}$ of 0.5 (the statistical ratio) and a spin-orbit splitting of 0.6 eV. In order to fit the Si $2p_{3/2}$ spectra, each chemical state is represented by a Gaussian convoluted by a Lorentzian of 0.1 eV full width at half-maximum (FWHM). [The broader C $1s$ spectra are simply fitted by sums of pure Gaussian components.] In the least-square fitting routine, we fix the Gaussian FWHM for each chemical state and in most cases BE positions are free parameters.

The zero binding energy is taken at the leading edge of the Si(111)-7×7 adatom surface states (the surface is metallic[19]). The bulk silicon Si $2p_{3/2}$ line is then found at 99.40 ± 0.05 eV and the adsorbed molecule C $1s$ line at 284.0 ± 0.1 eV.

C. X-ray absorption spectroscopy

C K-edge measurements are taken at different angles between the normal to the sample surface and the polarization vector of the radiation, in the range from $\theta=90°$ (normal incidence) to $\theta=10°$ (grazing incidence). The absorption was determined by collecting the total electron yield from the sample as a function of the photon energy. The detection consists of collecting electrons from the sample on an electron multiplier (dynode). The x-ray beam after the monochromator goes through a metal grid, which can serve as reference monitor. However because of C containing adsorbates on the grid, having their own XAS spectra in the range of interest, we follow a normalization procedure already proposed by Stöhr.[20] We divide the spectrum of surface *plus* adsorbate by the spectrum of the clean surface alone. Indeed, the absorption features of the grid are useful energy references to check any shift from one measurement to another. The absolute energy precision is estimated to ±0.2 eV.

III. RESULTS AND DISCUSSION

A. Adsorption at 300 K: Electronic structure and orientational order

We begin this section by examining how the surface states of the Si $2p$ core-level and valence-band (VB) lines ''feel'' the adsorption of the acetylene molecule at room temperature (Fig. 2). As the exposure increases one sees [Fig. 2(a)] that the intensity of the Si $2p$ line, attributed to the restatoms.[21] (RA's) and situated at -0.75 eV from the bulk silicon one, gradually decreases with increasing exposure. We do not observed any shift of the bulk silicon line larger than 0.05 eV upon acetylene adsorption. From an exposure of ~3000 L all the restatoms are quenched. Parallel to changes in the Si $2p$ spectra, the two surface states of the VB [Fig. 2(b)], attributed,[19] respectively, to the RA, at ~0.8 eV, and to the adatoms (AD's), at the Fermi level, disappear in a concerted manner.[22] This means that both restatoms and adatoms participate to the bonding with the molecule. STM (Ref. 2) has already evidenced that the electronic structure of the adatoms is modified after acetylene adsorption. The LEED patterns (not shown) indicate that adatom positions are also changed by the chemisorption process. Indeed after saturation of the surface, nonintegral spots disappear, except the six nearest spots around an integral spot [with coordinates $(p+k,q+l)$ where p,q are integral numbers and $k=0,\pm1/7$ and $l=0,\pm1/7$], which remain strong, and those spots distributed on the lines joining the 1×1 spots. This can be interpreted—as for the chemisorption of atomic H (Ref. 23)—in terms of a rearrangement of the adatoms on each triangular subunit of the DAS cell, leaving unaffected the corner holes and dimer walls in order to maintain the 7× periodicity. However, the role of the restatoms, which escaped to the previous STM measurement, is here clearly evidenced by photoemission. A new Si $2p_{3/2}$ struc-

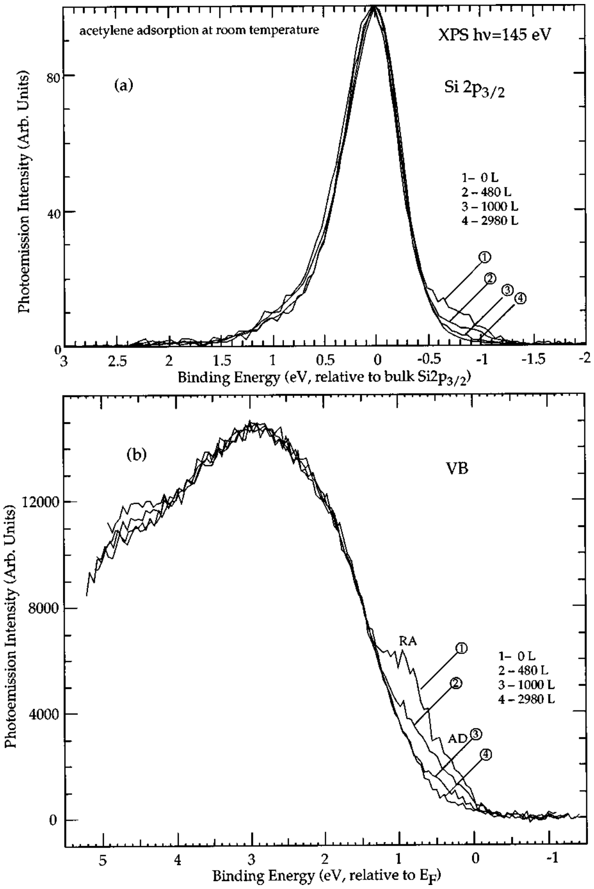

FIG. 2. (a) Si $2p_{2/3}$ core level and (b) valence-band spectra, measured at $h\nu=145$ eV, of a Si(111)-7×7 surface exposed to increasing doses of acetylene at 300 K ($P_{\text{acetylene}}=10^{-6}$ Torr).

ture, weak but measurable, grows at a binding energy higher than that of bulk Si, by $\sim+0.85$ eV. This line is attributed to the formation of a bond between a Si radical and the molecule.

A typical XPS C 1*s* spectrum obtained after an exposure of 4500 L at 300 K is presented in Fig. 3. The ‘‘clean’’ surface background—which contains a small contribution from SiC particles remaining even after repeated thermal cleanings at 1520 K—is subtracted to the molecule *plus* surface spectrum. The resulting curve is fitted by only one Gaussian peak of FWHM ~ 1.44 eV centered at 284 eV. This suggests the existence of only one kind of chemical bonding for the carbon atoms, and thus of only one bonding site. Taking a work function ϕ of 4.55 eV (the clean surface value, see Ref. 15 and references therein) the ionization potential IP of the adsorbed molecule is ~ 288.6 eV, ~ 2.5 eV smaller than the IP’s of free acetylene (291.1 eV), free ethylene (290.8 eV) or free ethane (290.7 eV).[24] The decrease in IP, passing from the free molecule to the adsorbed molecule, is indeed accounted for by a bonding shift (due to a net charge transfer between substrate and molecule[25]) and a relaxation shift.

The XAS C *K*-edge spectra of a surface exposed to 2980 L at 300 K is shown in Fig. 4. The dipole selection rules imply that the molecular orbital (MO) final state has a *p* orbital component. The resonance intensity associated with a specific MO final state is largest if the **E** vector points in the

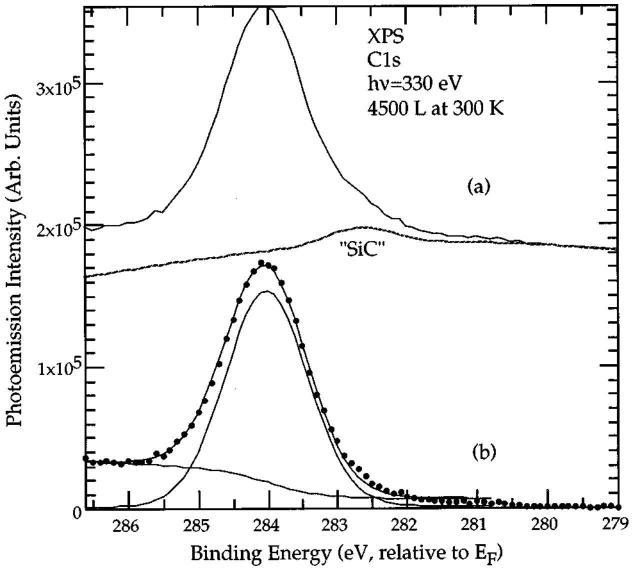

FIG. 3. (a) C 1*s* core-level spectra ($h\nu=330$ eV) of the substrate before exposure to acetylene (dashed line) and after exposure to 4500 L of acetylene ($P_{\text{acetylene}}=2.5\times10^{-6}$ Torr) at 300 K. (b) The acetylene C 1*s* spectra (dots) obtained after subtraction of the substrate ‘‘SiC’’ contribution and fit (solid line) by a Gaussian of FWHM equal to 1.44 eV.

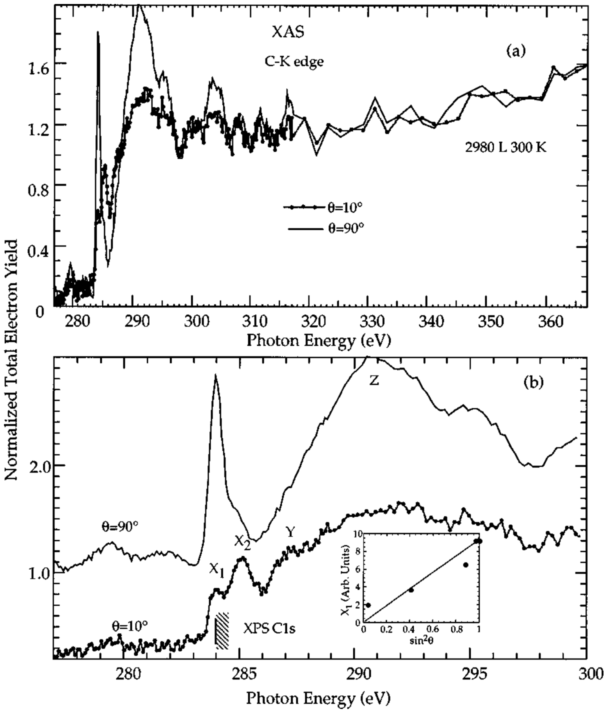

FIG. 4. (a) C *K*-edge absorption spectra of a surface exposed to 2980 L ($P_{\text{acetylene}}=10^{-6}$ Torr) of acetylene at 300 K, measured at $\theta=90°$ (**E** parallel to the surface plane) and $\theta=10°$ (**E** close to the normal to the surface plane). The curves are normalized to an equal ‘‘jump’’ before the absorption edge (275 eV) and ~ 80 eV after. (b) The near-edge region for $\theta=90°$ and 10° (the position of XPS C 1*s* is indicated). In inset we plot the intensity of peak X_1 as a function of $\sin^2\theta$ (additional data taken at angles between 10° and 90° are given).

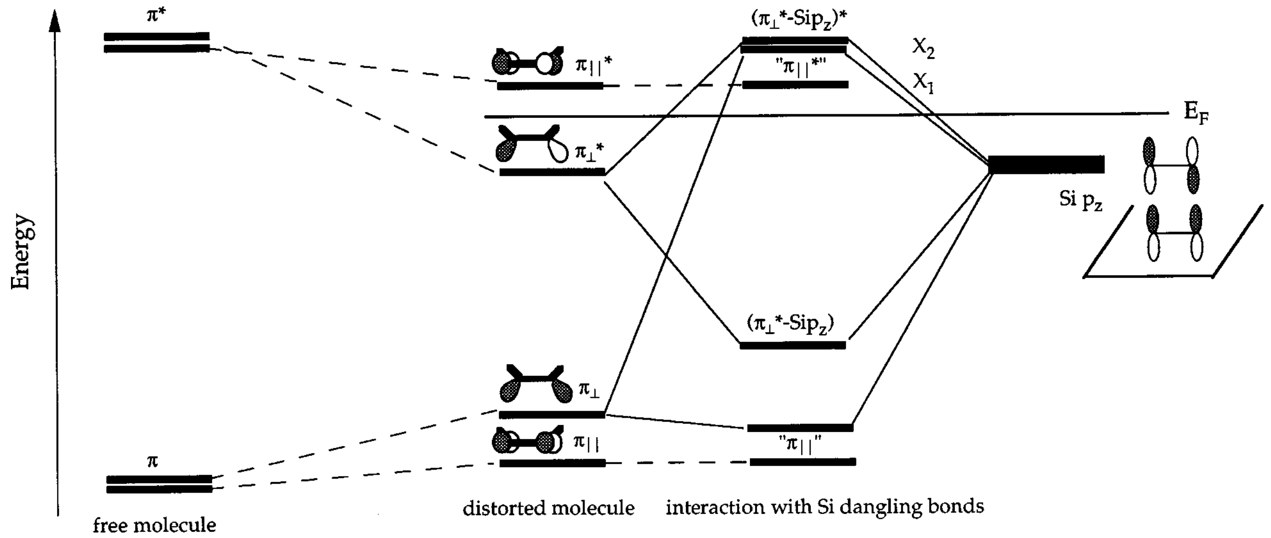

FIG. 5. Schematic orbital energy level correlation diagram of a di-σ bonded acetylene. For the linear molecule each π/π^* level is doubly degenerate. However, for a distorted acetylene (for simplicity *ethylenelike* with C_{2v} symmetry) the degeneracy is lifted. In-plane $\pi_\parallel$ and $\pi_\parallel^*$ are not much affected by the distortion and do not interact with Si orbitals. On the other hand, the bonding and antibonding ''$\pi_\perp$'' orbitals interact with Si p_z orbitals (forming a surface band). The occupied $\pi_\perp$ orbital hybridizes with Si p_z: the antibonding level $(\pi_\perp\text{-Si } p_z)^*$ is pushed up in energy above E_F and the electrons are dropped to the substrate (''donation''). The $\pi_\perp^*$ orbital decreases in energy to a position where it can hybridize strongly with Si p_z orbitals. The resulting bonding level $(\pi_\perp^*\text{-Si } p_z)$ can be filled by electrons coming from the substrate (''backdonation''), while the antibonding one $(\pi_\perp^*\text{-Si } p_z)^*$ passes over E_F. Peak X_1 and peak X_2 are attributed to $1s \rightarrow \pi_\parallel^*$ and $1s \rightarrow (\pi_\perp^*\text{-Si } p_z)^*$ transitions, respectively [the antibonding level $(\pi_\perp\text{-Si } p_z)^*$ having mainly Si p_z character].

direction of that MO, and the intensity vanishes if **E** is perpendicular to the direction of that orbital.[26]

Let us first examine the peaks that appear below IP, i.e., the bound states. At normal x-ray incidence ($\theta = 90°$, **E** parallel to the surface), the C_2D_2 dosed surface exhibits a strong π^* resonance at 283.9 eV (peak X_1). At grazing incidence ($\theta = 10°$, **E** close to the normal to the sample surface) one observes distinctively another π^* resonance at 284.9 eV (peak X_2) while the peak X_1 intensity weakens. The angular dependence of the two π^* resonances is explained as follows. If the molecule lies down on the surface, one π orbital of acetylene (''$\pi_\parallel$''), parallel to the surface, interacts weakly with the substrate, while the other one (''$\pi_\perp$'') is perpendicular to the surface and hence can rehybridize with Si radicals. A schematic orbital energy level correlation diagram, inspired by Hoffmann's approach[27] to the problem of molecular bonding on a surface, is given in Fig. 5. Peak X_1 will correspond to a $1s \rightarrow \pi_\parallel^*$ transition and X_2 to a $1s \rightarrow (\pi_\perp^*\text{-Si } p_z)^*$, where $(\pi_\perp^*\text{-Si } p_z)^*$ is the antibonding level resulting from the mixing of Si p_z orbitals (in the chosen coordinate system, x and y define the surface plane, and z is normal to it) with the $\pi_\perp^*$ orbital. We attribute peak Y situated at ~287 eV to a C-H* resonance, in analogy with the C K-edge spectra of ethane, ethylene, and acetylene adsorbed on noble metals compiled by Stöhr.[28]

These are the major trends. However, a careful examination of Fig. 4 shows that, at normal incidence ($\theta = 90°$), the intensity of structure X_2, is not strictly zero. This is not surprising, if one considers that the C p-like part of $(\pi_\perp^*\text{-Si } p_z)^*$ is certainly not exactly perpendicular to the C-C axis [see the antibonding b_1 orbital of C_2H_4 di-σ bonded to Pt(111)].[29] That is why a residual X_2 intensity at $\theta = 90°$ is not a definite proof a slight tilting of the C-C axis with respect to the surface plane, and hence of a molecule bridging a restatom and an adatom. [Adatoms are about 1 Å upward with respect to restatoms:[30] the C-C molecular axis would then be tilted by ~13° with respect to the surface plane, if the Si/C-C Si structure has equal SiCC angles and equal Si-C bond lengths.] In the inset of Fig. 4, we report the plot of peak X_1 intensity—obtained after subtraction of a step at E_F, taken at 284 eV, the position of the C 1s BE peak—as a function of $\sin^2 \theta$. It should be a straight line passing through zero if the $\pi_\parallel^*$ orbital was strictly oriented parallel to the surface.[31] The discrepancy (at grazing incidence) may come in part from uncertainties in measuring the intensity, in relation with Fermi-level step positioning and subtraction, but it may also arise from the distortion of the molecule that would adopt a symmetry still lower than that of ''ethylenic'' distorted molecule, where the C hybridization would then be close to sp^3 as suggested by HREELS data.[1]

Broad structures are also observed above IP. A prominent one, denoted Z in Fig. 4, is found around 291 eV. Its intensity strongly decreases for $\theta = 10°$, that is when **E** is nearly perpendicular to the CC axis of molecules lying down on the surface. This suggests that peak Z is related to transitions of 1s electrons into σ^* orbitals. We shall not make any attempt to deduce a carbon-carbon distance from the energy position of peak Z using the empirical method termed ''bond lengths with a ruler.'' [32] for the following reasons. As indicated by Piancastelli *et al.*,[33] in the K-shell absorption spectra of the dicarbons, the attribution of structures above IP is far from being unambiguous, as multielectron transitions as well as σ^* shape resonances can be observed; moreover, the correlation between the energy position of a σ^* resonance and the bond length, *taken as a single variable*, is also open to criticism.[33,34]

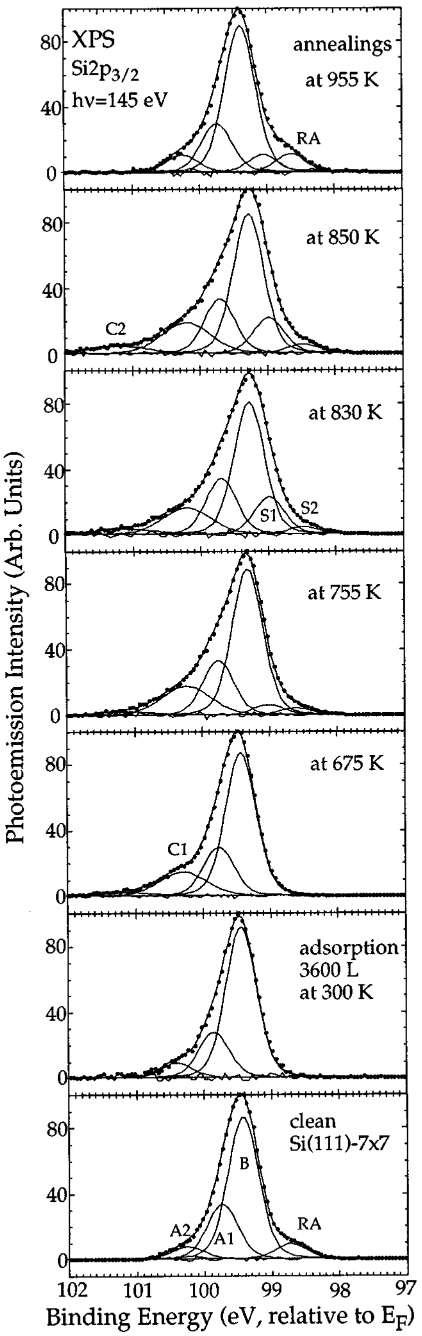

FIG. 6. Experimental Si $2p_{3/2}$ core level (dots) of a surface previously exposed to 3600 L of acetylene at 300 K ($P_{\text{acetylene}} = 10^{-6}$ Torr) and submitted to isochronal annealings (of 1 mn each). The corresponding fits (solid curves) are also given. The Gaussian FWHM is 0.48 eV for components B,RA,A_1,A_2,S_1,S_2, 0.79 eV for C_1, and 1.0 eV for C_2 (the Lorentzian FWHM is 0.1 eV for all components).

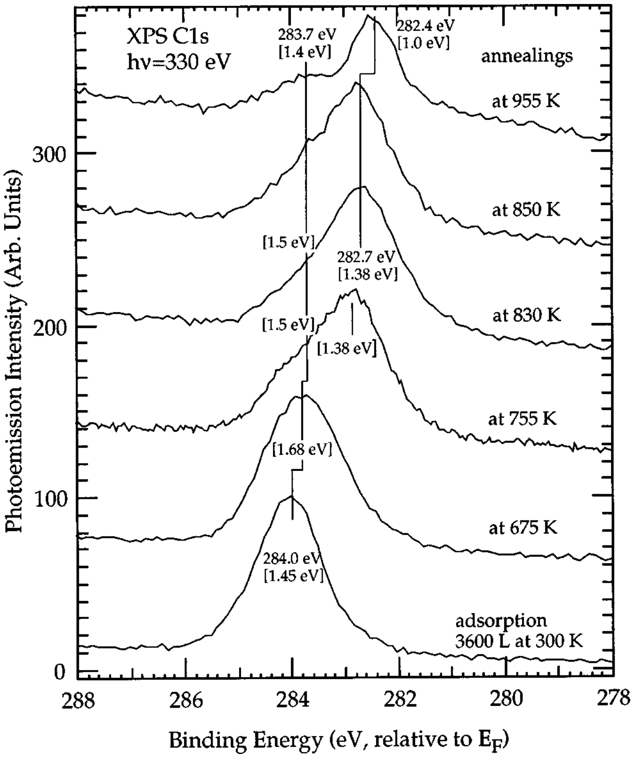

FIG. 7. C 1s core-level spectra of a surface previously exposed to 3600 L of acetylene at 300 K and submitted to isochronal annealings (of 1 mn each). The FWHM of each fitting component is given between brackets.

B. Thermal behavior of chemisorbed acetylene

The thermal stability of acetylene on Si(111)-7×7 is studied by performing successive isochronal (1 mn) annealing of a surface previously exposed to 3600 L of acetylene at room temperature. The XPS core-level spectra (Si 2p and C 1s) and XAS C K-edge spectra are recorded at room temperature after each annealing step.

The Si $2p_{3/2}$ and C 1s spectra are given in Figs. 6 and 7, respectively. The Si $2p_{3/2}$ spectrum of the clean surface (Fig. 6) is fitted by a bulk line (B) and by three other components, attributed to surface or near surface atoms:[35] the RA line at -0.78 eV, and two lines, A_1 and A_2 situated at $+0.33$ and $+0.9$ eV from B, respectively. A_1 is a mere help for curve fitting, as it contains various unresolved contributions, included that of the adatoms; A_2 has not received yet a definite attribution.[21,35] As discussed before the essential consequence of C_2D_2 adsorption at room temperature is the quenching of the RA line. Upon annealing in the 675–850 K temperature range, component C_1 grows at $+0.90 \pm 0.04$ eV from B, while an A_1 line centered at 0.36 ± 0.03 eV from B is still necessary to obtain a good fit. After the 850 K annealing step, a weak broad line C_2, at $+1.95$ eV from B must also be added. At 755 K and above two components, S_1 and S_2 (at -0.3 and -0.75 eV from B, respectively) have to be introduced to fit the low BE side of the bulk line. At 955 K, a drastic change occurs in the spectral weight as the Si $2p_{3/2}$ spectrum ressembles that of a clean surface: in particular, the C_1 component is strongly reduced (C_2 is even eliminated) and S_2 increases. The relative spectral weights of components C_1, S_1, S_2 as a function of temperature are reported in Fig. 8(a). The S_2 line very likely corresponds to the restatom line, because its binding energy is the same as that of the RA line of the clean surface, and because its weight after the 955 K annealing step is 7.5% of the total spectral weight, close to 6–7 % measured for clean-surface RA. Consequently, RA dangling bonds reappear on the surface from temperatures around 750 K.

However, it is more difficult to give a definite assignment to the other lines C_1, C_2, and S_1. Studying the thermal stability of adamantane on Si(111)-7×7 at 525 K, Simons

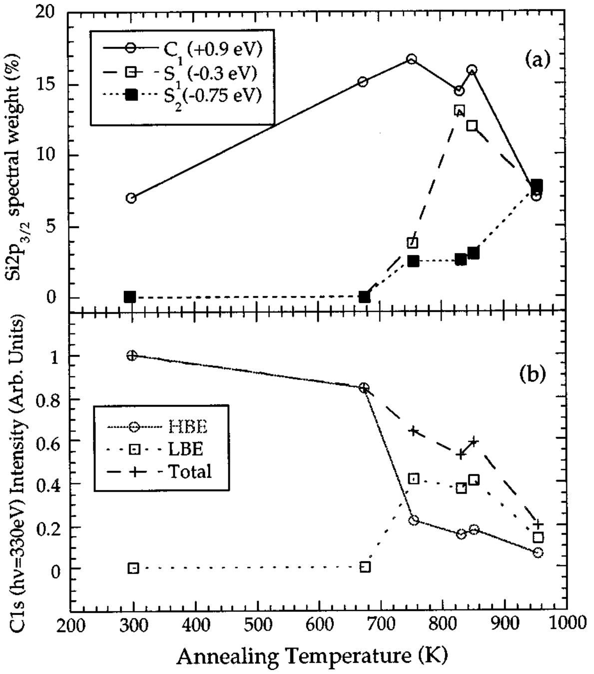

FIG. 8. (a) Variations of the Si $2p_{3/2}$ components (C_1, S_1, and S_2) and (b) of the C 1*s* components (HBE, LBE, and total) as a function of the annealing temperature.

et al.[36] have fitted their Si 2*p* spectra with three components at +0.48 eV, +0.98 and +1.48 eV from the bulk line, attributed to a Si atom having an increasing number of more electronegative C ligands[37] around it (from one to three). However, the interpretation of the chemical shifts of silicon with carbon seems to be more complicated that this simple picture might suggest. Indeed upon molecular chemisorption at room temperature, where a single bond is formed between one Si dangling bond and one carbon atom, the chemical shift is ~+0.9 eV. It has also been shown recently[38] that the Si 2*p* shift between bulk silicon and thermally grown 3C-SiC—in this zinc-blende structure each Si atom has four C ligands—is a function of the carbide overlayer thickness. For ultrathin carbide films of about 40 Å, for which band bending effects and/or charge effects are minimized, the carbide is shifted by ~+0.9 eV from the substrate line. Consequently, we doubt that the additivity of the chemical shifts (0.48 eV per C ligand) proposed by Simons *et al.* is a valid hypothesis, as the energy distance between bulk silicon and carbide should be around +2 eV, which is not observed. We rather believe, that the C_1 component corresponds to the bonding of silicon with different carbon moieties, that is, the bonding between Si and C_2D_2 or C_2D_x $(x<2)$, or between Si and atomic carbon. Consequently, any progress in the interpretation of the Si 2*p* core levels needs an examination of the corresponding C 1*s* core levels of Fig. 7.

Heating at 675 K already induces changes in the line shape of the C 1*s* spectrum obtained after room-temperature adsorption. A slight shift of the single component to lower BE (by ~−0.25 eV) and a broadening are observed. After annealings at 755 K and above, all the recorded spectra exhibit two distinct components separated by 1–1.3 eV. In Fig. 8(b), we have plotted, as a function of temperature, the intensities of the high binding energy (HBE, 284–283.7 eV range) and of the low binding energy (LBE, 282.7–282.4 eV) components, respectively, and the sum of both. The HBE component can be reasonably attributed to adsorbed C_2D_2, decomposed C_2D_x $(x<2)$, or pure C compounds. Because of the difference in electronegativity between Si and C, the LBE component is attributed to atomic C having Si first neighbors.[38] If one considers the behavior of the overall C 1*s* intensity (total), we observe a ~15% loss after the 675 K annealing step. Then for the successive steps the total C 1*s* intensity decreases strongly: after the 955 K step, it is only 1/5th of the initial value.

However, we observe that the C 1*s* LBE component intensity is constant in the 755–850 K temperature range, like the C_1 component of the Si $2p_{3/2}$ level. The kinetic energy of both C 1*s* and Si 2*p* photoelectrons is the same (~46 eV), and such is the probed depth. Identifying the LBE component of C 1*s* at 282.7 eV with the C_1 component of Si $2p_{3/2}$ at 100.1 eV, the energy distance, independent of any energy reference, is ~182.6 eV, a value compatible with those found for $Si_{1-x}C_x$ $(x \leqslant 1)$ thin films on Si: this energy distance decreases from 182.7 to 182.3 eV with increasing x according to Ref. 38. The distance between the C 1*s* LBE component and Si $2p_{3/2}$ component C1 is further reduced to 182.2 eV after the 955 K step. This could correspond to the formation of 3C-SiC precipitates, and the reduced FWHM (see Fig. 7) of this LBE C 1*s* component would manifest their more chemically ordered structure.

If the C 1*s* spectra give valuable informations on the formation of silicon-carbon compounds, through the appearance of the LBE component, little can be said about the nature of the carbon compounds, resulting from the molecule decomposition, to which the HBE component is attributed. In such a case the XAS C *K*-edge spectra, presented in Fig. 9 will be much more informative. At a given position of the polarization vector **E** [$\theta=40°$, Fig. 9(a)], the π^* and C-H* region is particularly affected by the thermal annealing. After the 675 K annealing step, while peak Y does not change, peak X_1 is strongly reduced with respect to X_2. Measurement at normal and grazing incidence (not shown) indicate that X_1 is still polarized in the surface plane and X_2 in a direction normal to this plane. The decrease of X_1 upon annealing may suggest that the in-plane $\pi_\parallel^*$ orbital, because of a molecular rearrangement, is passing below E_F and is being filled with electrons. A more likely explanation is that the $\pi_\parallel$ orbital opens and that new bonds are formed with C atoms (polymerization) or Si atoms. [The absence of interaction of $\pi_\parallel$ with a flux of Si atoms at 300 K will be shown in Sec. III C.] We note also that dehydrogenation does not occur yet as peak Y remains strong. The XAS spectrum taken at $\theta=40°$ after the 755 K annealing step is still structured. An angle-dependent study [Fig. 9(b)] shows that the peak at ~285 eV (continuing X_2) is still polarized along the normal to the surface plane. However, peak X_1 has disappeared—there is still a step at the Fermi level—as well as peak Y. The latter point agrees with the observation made by Yoshinobu *et al.*[1] that molecular dehydrogenation begins at 750 K, as a Si-H vibrational mode shows up. The subsequent annealing at 830 K leads to an unstructured absorption edge presenting no polarization effects.

Using XPS Si 2*p*/C 1*s* and XAS C *K*-edge data altogether gives us the possibility of writing a plausible scenario

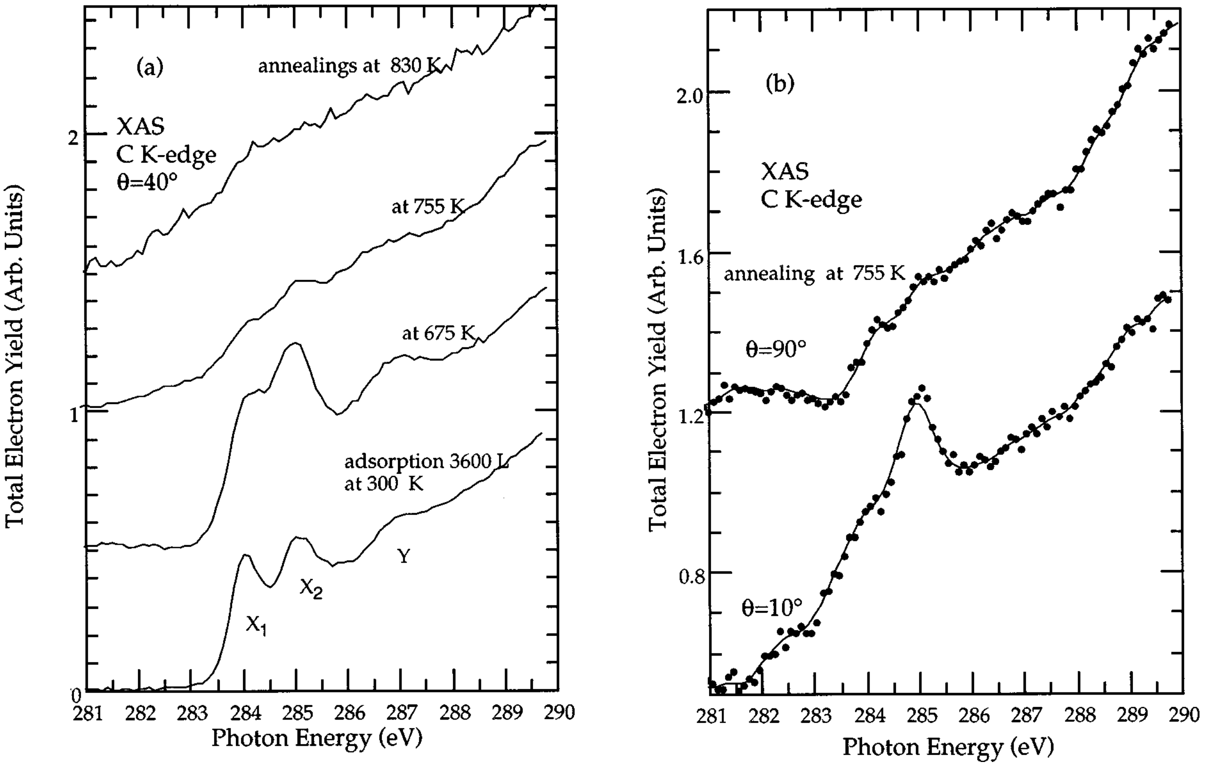

FIG. 9. (a) C K-edge spectra ($\theta = 40°$) of a surface previously exposed to 3600 L of acetylene at 300 K and submitted to isochronal annealings (of 1 mn each). (b) C K-edge spectra of the surface after the annealing step at 755 K, taken at $\theta = 90°$ (**E** parallel to the surface plane) and $\theta = 10°$ (**E** close to the normal to the surface plane).

for the thermal behavior of acetylene on Si(111)-7×7. (i) $T = 300$ K: the molecule is di-σ chemisorbed at the surface. (ii) $T = 675$ K: a small fraction of the molecules may desorb. For the remaining molecules the bonding configuration of the in-plane molecular π orbital changes. Acetylene polymerization can be envisaged: with an increased temperature the motion of the molecules over the surface is facilitated and the in-plane π bond opens to permit molecular addition. (iii) $T = 755$ K: the molecular dehydrogenation is evidenced, the in-plane ''π'' component disappears, while the out-of-plane one is conserved. This may be the hint of a graphitization process, the graphite sheets being parallel to the surface plane. In the meanwhile, C atoms are liberated and find subsurface dissolution sites, which provokes a decrease of the total C 1s signal. Nude areas reappear as the restatom component is seen again. The S_1 component of Si $2p_{3/2}$ can be attributed to new silicon surface states that are filled up by electrons, because of changes in the band structure due to C dissolution. (iv) $T = 830-850$ K: The sp^2 ''graphitic'' carbon is changed into a sp^3 carbon compound. H has already desorbed from the surface at 800 K,[39] and more atomic carbon penetrate into the silicon surface planes. The intensity of the silicon surface state S_1 is then maximum. Its spectral weight of 13–14 % would correspond to a density of C-induced surface states equal to twice that of the restatoms. This situation could correspond to the so-called C-stabilized Si(111)-1×1 surface described by McPherson *et al.*[40] from their LEED and thermal desorption study of cyclohexene on Si(111)-7×7: such a surface formed after a desorption cycle ending at 925 K would contain more dangling bonds than the clean surface, because of its enhanced catalytical reactivity. (v) $T = 955$ K: Carbon

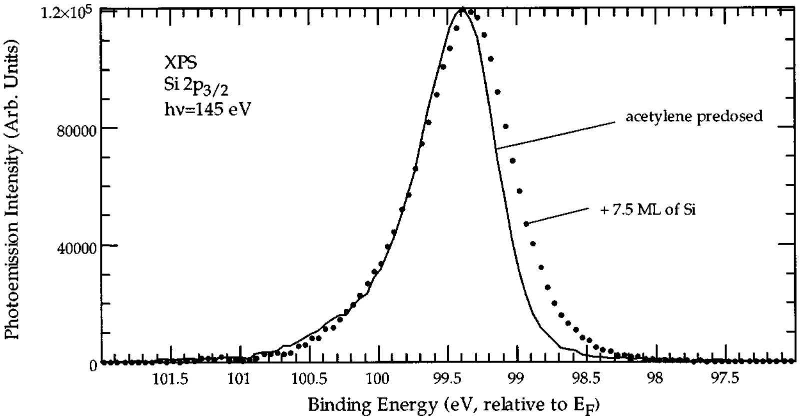

FIG. 10. Solid line: Si $2p_{3/2}$ spectrum of an acetylene predosed surface (300 K, 4500 L, $P_{\mathrm{acetylene}} = 2.5 \times 10^{-6}$ Torr). Dots: Si $2p_{3/2}$ spectrum of the predosed surface after deposition of 7.5 ML of silicon at 300 K.

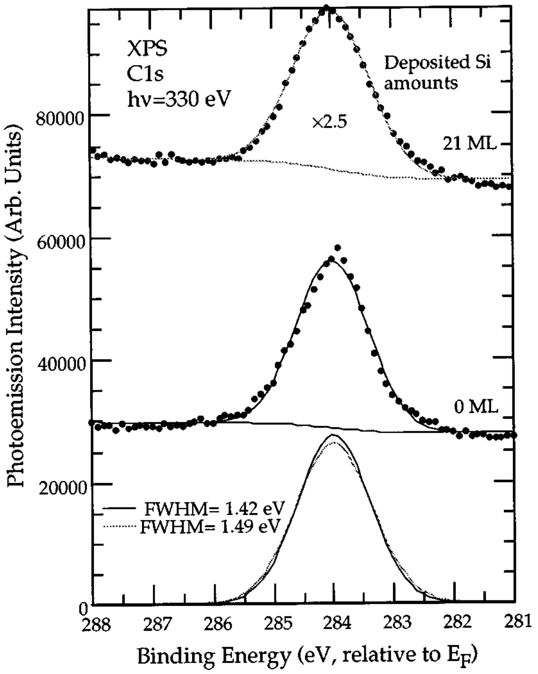

FIG. 11. Top: C 1*s* spectrum of the acetylene predosed surface after deposition of 21 ML of silicon. Middle: C 1*s* spectrum before Si deposition. Bottom: comparison of the C 1*s* fitting Gaussians of the acetylene predosed surface, before exposure to the Si flux (black line) and after (grey line).

atoms dissolve more deeply into the silicon lattice on the one hand, and form carbide precipitates on the other hand. A pure carbon compound (nongraphitic) remains on the surface. These observations are in excellent accord with our previous data[38] on the carbonization of Si(001) at 1090 K by acetylene.

C. Room-temperature deposition of silicon atoms on C_2D_2 precovered Si(111)-7×7

The Si $2p_{3/2}$ spectra of an acetylene predosed Si(111)-7 ×7 surface (4500 L) exposed also to a silicon flux do not change appreciably, at least up to 2 ML of deposited Si. For larger Si deposits (7.5 ML, Fig. 10), one observes a broadening of the spectrum at BE's lower than the bulk line, but not at higher BE's, which would have indicated the formation of a silicon-carbon compound. The absence of formation of silicon-carbon compounds is confirmed by the C 1*s* spectra, which do not change in shape or position for increasing deposited amounts: the spectrum given in Fig. 11 (obtained after the deposition of 21 ML of silicon) exhibits no state at ~282.5 eV characteristic of a C atom having four Si neighbors (see Sec. III B). On the other hand, the absolute intensity of the C 1*s* signal decreases with increasing deposited Si amounts at a rate of 3% per 1 ML of deposited silicon. The XAS C *K*-edge spectra confirm that the electronic structure of the molecule is not much affected by Si deposition. Typical spectra at glancing and normal incidence are given in Fig. 12. They correspond to a Si deposition of 2 ML, but spectra taken after longer exposures to Si flux are similar.[41] The π^* part of the absorption spectrum still exhibits a two-peaked structure: X_1 is still strongly polarized in the sample plane and X_2 in a direction perpendicular to it. There is no hydrogen abstraction by incoming Si atoms as peak *Y* is still visible.

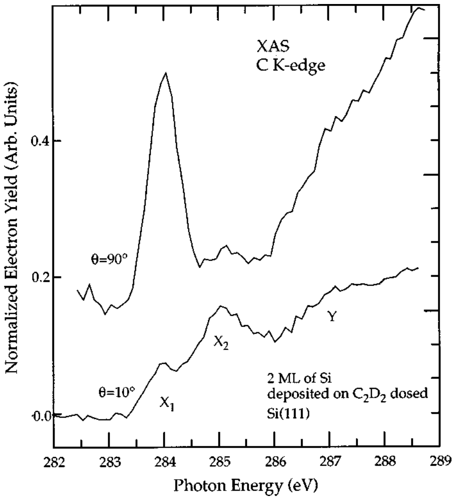

FIG. 12. C *K*-edge spectra of the acetylene predosed surface after deposition of 2 ML of silicon, taken at $\theta = 90°$ (**E** parallel to the surface plane) and $\theta = 10°$ (**E** close to the normal to the surface plane).

Consequently the C 1*s* intensity decrease has to be ascribed to a loss of C_2D_2, whose desorption is stimulated by the Si flux. Once deposited on a *clean* Si(111)-7×7 surface at 300 K, silicon atoms can break the backbonds of adatoms, as it has been proposed by Ichimiya, Nakahara, and Tanaka,[42] or can sit over a restatom site, as indicated by STM topographic images.[43] The disarrangement of both adatoms and restatoms which bond to new incoming Si atoms, could indeed favor some C_2D_2 desorption. Under an Si flux, the in-plane π bond of the molecule does not open to form Si-C bonds: the molecule manages to reform continuously a di-σ bonding configuration with surface silicon atoms, *floating* over the growing Si layer, with its C-C axis parallel to the sample surface.

IV. CONCLUSIVE REMARKS

The present paper discusses core-electron/valence-band photoemission spectra and absorption-edge spectra of acetylene chemisorbed on Si(111)-7×7. Such spectra contain a wealth of information on this adsorbate/substrate system, which has been until now studied essentially by vibrational spectroscopies or topographic tunneling microscopy.

Upon adsorption at 300 K, the Si 2*p* core-level and valence-band spectra show that the electron occupancy of both adatoms and restatoms is modified. The C 1*s* line is fitted with a single component, which is indicative of a single bonding site. The alignment of the C-C molecular axis by the chemisorption bond leads to strong polarization dependence of the C *K*-edge spectra. This dependence is discussed within simple, but illustrative, molecular orbital schemes at hand. The orientation of the C-C molecular axis is then determined to be nearly parallel to the surface plane. The precise measurement of a tilt angle, which would give evidence for a di-σ bridge between close neighbor adatoms and restatoms appears to be out of reach, because of a possible ''rotation'' of the ''π^*'' molecular orbitals.

The stability of the molecule and the correlative modification of silicon chemical environment is studied by performing thermal annealings of an acetylene-saturated surface. With increasing temperature, we find hints that the molecule first polymerize, then forms a graphitelike compound after dehydrogenation, and finally produces a nongraphitic pure carbon compound. In parallel, atomic carbon is released and penetrates into the substrate inducing the formation of silicon-carbon compounds and new silicon surface states. Evidences for SiC precipitates are found only at 950 K. There is a narrow temperature window (750–850 K) in which nonstoichiometric $Si_{1-x}C_x$ compounds are likely to be formed. The molecule remains chemically stable at 300 K in the presence of an external Si source, floating over the growing Si layer with no appreciable changes in its electronic structure. In particular the C K-edge spectra exhibit the same polarization dependence of the two π^* peaks before and after Si deposition.

Is the distance between radicals to which the molecule is di-σ bonded, a parameter determining the conformation of the molecule, i.e., its hybridization? If the interpretation of the HREELS data of Refs. 1 and 4 is correct, apparently the C-C distance would be the same on Si(001)-2×1 (Si-Si distance between 2.3 and 3.8 Å) and Si(111)-7×7 (Si-Si distance around 4.5 Å). Then this may significate that a severe rearrangement of the surface Si adatoms occurs on the 7×7 surface. This is indeed suggested by the LEED patterns, although, according to Yoshinobu *et al.*,[2] the STM images do not show a significant displacement of the adatoms. For our part, we agree with McPherson and co-workers[40] when they state that STM is capable of resolving the basic features of the DAS structure (that is the corner holes and dimer walls), *but cannot be used to rule out a possible reconstruction within the unit cell*. Thus one has to envisage the possibility of a displacement of the adatom toward the restatom, or even that of a bridge site formed by a restatom and a ''pedestal'' atom (see Fig. 1, the Si-Si distance would be reduced to 3.8 Å, but one of the Si atoms would be hypervalent). Unfortunately we lack calculations of the absorption geometries of acetylene on the ''real'' 7×7 surface, or on a realistic simplification of this reconstruction, although this has been already done with success for the adsorption of O_2.[44]

ACKNOWLEDGMENTS

We are indebted to Professor M. Tronc for discussions and comments. Some of this work was supported by the Brazilian CNPq and the French CNRS-GDR86.

---

*Electronic address: roch@ccr.jussieu.fr

†Present address: Departamento de Física Aplicada C-XII, Universidad Autónoma de Madrid, Cantoblanco, E-28049, Madrid, Spain.

[1] J. Yoshinobu, H. Tsuda, M. Onchi, and M. Nishijima, Chem. Phys. Lett. **130**, 170 (1986).

[2] J. Yoshinobu, D. Fukushi, M. Uda, E. Nomura, and M. Aono, Phys. Rev. B **46**, 9520 (1992).

[3] M. N. Piancastelli, R. Zanoni, D. W. Niles, and G. Margaritondo, Solid State Commun. **72**, 635 (1989).

[4] M. Nishijima, J. Yoshinobu, H. Tsuda, and M. Onchi, Surf. Sci. **192**, 383 (1987).

[5] C. Huang, W. Widdra, X. S. Wang, and W. H. Weinberg, J. Vac. Sci. Technol. A **11**, 2250 (1993).

[6] Y. Chen, Z. Liu, Q. Zhang, K. Feng, and Z. Lin, Appl. Phys. Lett. **67**, 2936 (1995).

[7] T. Yoshinobu, M. Nakayama, H. Shiomi, T. Fuyuki, and H. Matsunami, J. Cryst. Growth **99**, 520 (1990).

[8] M. Kitabatake and J. E. Greene, Jpn. J. Appl. Phys., Part 1 **35**, 5261 (1996).

[9] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).

[10] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).

[11] M. N. Piancastelli, N. Motta, A. Sgarlata, A. Balzarotti, and M. De Crescenzi, Phys. Rev. B **48**, 17 892 (1993).

[12] Q. Liu and R. Hoffmann, J. Am. Chem. Soc. **117**, 4082 (1995).

[13] Y. Imamura, Y. Morikawa, T. Yamasaki, and H. Nakatsuji, Surf. Sci. **341**, L1091 (1995).

[14] B. Weiner, C. S. Carmer, and M. Frenklach, Phys. Rev. B **43**, 1678 (1991).

[15] F. J. Himpsel, B. S. Meyerson, F. R. McFeely, J. F. Morar, A. Taleb-Ibrahimi, and J. A. Yarmoff, in *Proceedings of the Enrico Fermi School on Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation*, edited by M. Campagna and R. Rosei (North Holland, Amsterdam, 1990), p. 203.

[16] J. Stöhr, in *NEXAFS Spectroscopy*, edited by R. Gomer, Springer Series in Surface Science, Vol. 25 (Springer-Verlag, Berlin, 1992).

[17] B. S. Schwartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).

[18] F. Rochet, C. Poncey, G. Dufour, H. Roulet, W. N. Rodrigues, M. Sauvage, J. C. Bouliard, F. Sirotti, and G. Panaccione, Surf. Sci. **326**, 229 (1995).

[19] G. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988).

[20] J. Stöhr, in *NEXAFS Spectroscopy*, edited by R. Gomer, Springer Series in Surface Science, Vol. 25 (Springer-Verlag, Berlin, 1992), p. 157.

[21] C. J. Karlsson, E. Landemark, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. B **50**, 5767 (1994).

[22] The same observation was made by Carbone and co-workers [M. Carbone, R. Zanoni, M. N. Piancastelli, G. Comtet, G. Dujardin, L. Hellner, A. Mayner, J. Electron Spectrosc. Relat. Phenom. **76**, 271 (1995)] during the adsorption of *ethylene* on Si(111)-7×7.

[23] C. J. Karlsson, E. Landemark, L. S. O. Johansson, U. O. Karlsson, and R. I. G. Uhrberg, Phys. Rev. B **4**, 1521 (1990) and references therein.

[24] A. P. Hitchcock and C. E. Brion, J. Electron Spectrosc. Relat. Phenom. **10**, 317 (1977).

[25] For acetylene adsorbed on a di-σ site of a non-reconstructed ''ideal'' Si(111) surface (Si-Si distance of 3.8 Å) the molecule charge is $-0.27e$, because of a strong backdonation from surface Si radicals to the π_1^* orbital [S.-Y. Chu and A. B. Anderson, Surf. Sci. **194**, 55 (1988)].

[26] J. Stöhr, in *NEXAFS Spectroscopy*, edited by R. Gomer, Springer Series in Surface Science, Vol. 25 (Springer-Verlag, Berlin, 1992), pp. 69–72.

[27] R. Hoffmann, *Solids and Surfaces, a Chemist's View of Bonding in Extended Structures* (VCH, New York, 1988).

[28] J. Stöhr, in *NEXAFS Spectroscopy*, edited by R. Gomer, Springer Series in Surface Science, Vol. 25 (Springer-Verlag, Berlin, Heidelberg, 1992), p. 268.

[29] J. Stöhr, in *NEXAFS Spectroscopy*, edited by R. Gomer, Springer Series in Surface Science, Vol. 25 (Springer-Verlag, Berlin, 1992), p. 316.

[30] S. Y. Tong, H. Huang, C. M. Wei, W. E. Packard, F. K. Men, G. Glander, and M. B. Webb, J. Vac. Sci. Technol. A **6**, 615 (1988).

[31] For a 1*s* initial state and a *vector* final state orbital the transition intensity (the polarization factor is 1 for an undulator) is proportional to $2\cos^2\theta\cos^2\alpha+\sin^2\theta\sin^2\alpha$ on a threefold or higher symmetry substrate (α is the polar angle measuring the orientation of the final state). If $\pi^*_{\parallel}$ is strictly contained in the surface plane, $\alpha=90°$ and the transition intensity is proportional to $\sin^2\theta$. [J. Stöhr, in *NEXAFS Spectroscopy*, edited by R. Gomer, Springer Series in Surface Science, Vol. 25 (Springer-Verlag, Berlin, 1992), p. 284.]

[32] J. Stöhr, F. Sette, and A. L. Johnson, Phys. Rev. Lett. **53**, 1684 (1984).

[33] M. N. Piancastelli, D. W. Lindle, T. A. Ferrett, and D. A. Shirley, J. Chem. Phys. **86**, 2765 (1987).

[34] J. Stöhr and co-workers (Ref. 32 of this paper) attribute to σ^* shape resonances peaks observed at 291.2, 301, and 310 eV, for free ethane, free ethylene, and free acetylene, respectively, and correlate empirically these energy positions to the C-C bond lengths. Then they apply the same rule to molecules adsorbed on surfaces. A substantial theoretical support to empiricism is provided by Sheehy and co-workers [J. A. Sheehy, T. J. Gil, C. L. Winstead, R. E. Farren, and P. W. Langhoff, J. Chem. Phys. **91**, 1796 (1989)]. Modeling the molecular potential along the symmetry axis of a molecule after a *one-dimensional* finite square well, these authors show that the molecular orbital energies for *virtual* states (that can be attained during *K*-shell photoionization) correlate with the square well energy formula $(\pi^2/2)\times(n^2/L^2)$ (in Hartree), where n is the square-well quantum number and L an *effective* well width related to the molecular bond lengths. However, the definition of the effective width L changes with the type of molecule: to give an example, L is equal to $R_{CC}+4R_{CH}$ for C_2H_2, while L equals $3R_{CC}$ for nonlinear molecules like C_2H_4 and C_2H_6, where R_{CC} and R_{CH} are carbon-carbon and carbon-hydrogen bond lengths, respectively. The one dimensional square well modelization, although appealing, may be too simplified to deal with such issues like the chemisorption of π hydrocarbons on Si(111)-7×7. In other terms, what is the shape (and width) of the potential for a $Si_2C_2H_2$ cluster?

[35] Ch. Poncey, F. Rochet, G. Dufour, H. Roulet, F. Sirotti, and G. Pannaccione, Surf. Sci. **338**, 143 (1995).

[36] J. K. Simons *et al.*, Surf. Sci. **346**, 21 (1996).

[37] In Pauling's electronegativity scale $\chi_{Si}=1.8$ and $\chi_C=2.5$ [L. Pauling, *The Nature of the Chemical Bond*, 2nd ed. (Cornell University Press, Ithaca, New York, 1945)].

[38] G. Dufour, F. Rochet, F. C. Stedile, Ch. Poncey, M. De Crescenzi, R. Gunnella, and M. Froment, Phys. Rev. B **56**, 4266 (1997).

[39] Ch. Kleint and K.-D. Brzoska, Surf. Sci. **231**, 177 (1990).

[40] C. D. McPherson, D. Q. Hu, M. Doan, and K. T. Leung, Surf. Sci. **310**, 231 (1994).

[41] At least up to 7.5 ML of deposited Si, for which the C 1*s* intensity is still 70% of the initial value, the π^* bound state peaks are sufficiently intense with respect to the edge step.

[42] Analyzing RHEED intensity rocking curves, Ichimiya and coworkers [A. Ichimiya, H. Nakahara, and Y. Tanaka, J. Cryst. Growth **163**, 39 (1996)] have shown that for Si deposited amounts smaller than or equal to 0.5 ML, the formation of a $\delta 7\times 7$ pattern is indicative of the disarrangement of adatoms on each triangular subunit of the DAS structure. Upon further deposition an amorphous film is formed over the $\delta 7\times 7$ structure, with no destruction of the underlying dimer-stacking fault framework.

[43] U. Köhler, J. E. Demuth, and R. J. Hamers, J. Vac. Sci. Technol. A **7**, 2860 (1989).

[44] B. Schubert, Ph. Avouris, and R. Hoffmann, J. Chem. Phys. **98**, 7593 (1993).